ically 0.6 mmol, were suspended in mesitylene and the stoichiometric quantity of cyclohexene or cyclooectene was added. Refluxing for 36 h failed to produce a reacion. Negative results were also found by Olah and Welch for Na_2UO_8.[26] However, refluxing of compound **15** (0.002 mol.) in allylalcohol for 20 h at 80 °C and subsequent cooling in dry ice–CCl_4 for 1 h produced the allylalcohol epoxide as monitored by TLC. This conclusion is supported by the proton NMR spectrum of the reaction product which shows narrow multiplets centered at 2.7, 3.1, and 3.6 ppm as required for allylalcohol epoxide.

Registry No. **1**, 78435-89-9; **2**, 16923-61-8; **3**, 24564-38-3; **4**, 64121-21-7; **5**, 78456-39-0; **6**, 78435-90-2; **7**, 78435-91-3; **8**, 78435-92-4; **9**, 78435-93-5; **10**, 78456-40-3; **11**, 78435-94-6; **12**, 78435-95-7; **13**, 78435-96-8; **14**, 78435-97-9; **15**, 78435-98-0; **16**, 78435-99-1; **17**, 78436-00-7; L, 1761-56-4; L′, 7361-93-5; 2-aminophenol, 95-55-6; salicylaldehyde, 90-02-8; 2-aminobenzoic acid, 118-92-3.

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Photochemistry of (Dioxygen)bis(triphenylphosphine)palladium in Chlorinated Hydrocarbon Solvents

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Received January 8, 1981

The photochemical reactivity of charge-transfer excited states has been a subject of increasing interest.[1-4] In order to probe the properties of metal to ligand charge-transfer excited states, we began an investigation of zerovalent, d^{10} palladium complexes with ligands having low optical negativity of the type PdL_4 (L = Ph_3, PPh_2Me) and PdL_2 (L = diphos). Because of the full d shell, the lowest energy electronic transitions involving the metal 4d orbitals are metal to ligand charge transfer. These complexes possess the additional properties of being simple to prepare and handle and of having a rich and well-characterized thermal chemistry.[5-8]

Early in the course of our investigations, we found that the compounds were highly photoactive in halogenated hydrocarbon solvents but did not give strictly reproducible results. Further investigation revealed that the photochemistry was very sensitive to the presence of trace amounts of oxygen and that the majority of reactions we observed originated from PdL_2O_2. In this note we report the photochemistry of PdL_2O_2 in dichloromethane solution.

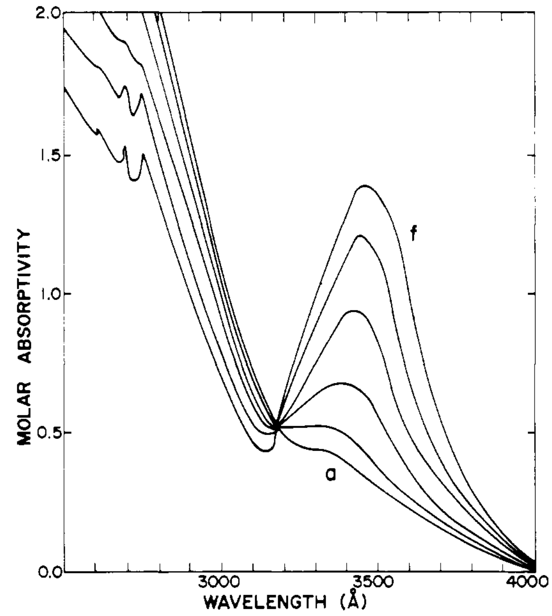

Figure 1. Spectral changes during irradiation of a 1.76 × 10^{-4} M solution of $Pd(PPh_3)_2O_2$ in dichloromethane: (a) no irradiation; (b) irradiation time of 15 s; (c) 30 s; (d) 60 s; (e) 90 s; (f) 120 s.

Experimental Section

Compounds. $Pd(PPh_3)_4$ was prepared from $PdCl_2$ and PPh_3[9] with use of the literature method.[9] $Pd(diphos)_2$ and $Pd(PPh_2Me)_4$ were prepared by adapting the same method with the use of appropriate ligands. The PdL_2O_2 complexes were prepared by the method of Wilkinson[7] while PdL_2Cl_2 was prepared by the method of Tayim.[8] All solvents were distilled at least twice before use and in some instances were degassed by blowing N_2 through the solvent followed by freeze–pump–thaw cycles.

Instrumentation. The electronic absorption spectra and the absorbance changes for the quantum yield measurements were taken with a Cary 14 spectrometer and a Hitachi PE 139 UV–visible spectrometer, respectively. Infrared absorption spectra were taken with a PE 521 grating IR spectrophotometer.

Photolysis was carried out with use of a Hanovia 1000-W high-pressure mercury–xenon lamp or a 100-W mercury lamp. The light from the 1000-W lamp was collimated and filtered to provide a parallel 405-nm beam. A transmission spectrum of the filtered light revealed that the 405-nm line was contaminated with a small amount of the 438-nm line. The 100-W lamp was selectively filtered with use of a 7-51 Corning filter and a $CuSO_4$ solution to provide 366-nm light.

Photochemistry. All photochemical reactions were studied with use of an optical bench to ensure constant geometry. The radiation was incident on a 1-cm Cary cell (3-mL capacity) which was encased in water-cooling system to limit heating effects. The solutions were stirred by a magnetic stir bar to ensure uniform illumination. The photon flux from the filtered lamp was measured with use of ferrioxalate actinometry.[10]

The quantum yield of product formation was obtained in two ways. The appearance of an intense absorption peak at 345 nm corresponding to PdL_2Cl_2 was monitored at intervals during the photolysis and the quantum yield then calculated. In addition, the PdL_2Cl_2 production was also monitored by collecting and weighing the photoproduct. Disappearance of the Pd complex was followed by monitoring an IR band on the PE 521.

Singlet O_2 analysis was performed with 1-methylcyclohexene as a detector trap.[11] In the presence of singlet O_2, 1-methylcyclohexene reacts to form three peroxo compounds:

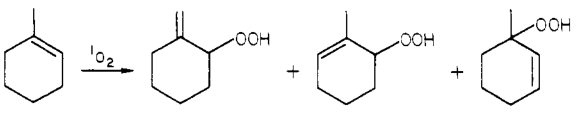

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Table I. Quantum Yields of PdL_2Cl_2 Formation

compd[a]	solvent (conditions)	quantum yield of PdL_2Cl_2 formation[b]
$PdL_2O_2 + 2L$	CH_2Cl_2 (degassed)	0.5[c]
$PdL_2O_2 + 2L$	CH_2Cl_2 (atmospheric O_2)	0.45[c]
$PdL_4 + O_2$	CH_2Cl_2 (atmospheric O_2)	0.5[c]
$PdL_4 + O_2$	CH_2ClCH_2Cl (atmospheric O_2)	0.5[c]
$PdL_4 + O_2$	chloroform (atmospheric O_2)	0.6[c]
$PdL_4 + O_2$	1,1-dichloroethane	0.5[c]
$PdL_4 + O_2$	$Ph:CH_2Cl_2$ 1:1 (O_2 gas)	0.5[c]
PdL_2O_2	CH_2Cl_2 (degassed)	no reaction[c]
$PdL_2O_2 + 2L$	CH_2Cl_2 (atmospheric)	no reaction[d]

[a] $L = Ph_3P$. [b] Experimental uncertainties are ±0.2. [c] Irradiated at 405 nm. [d] Irradiated at $\lambda > 500$ nm.

10^{-2} M benzene and acetonitrile solutions of both methylcyclohexene and $Pd(PH_3)_2O_2$ were used. After illumination, BH_4^- was added to reduce any peroxo compound to the corresponding alcohol in order to allow separation on an high-pressure chromatograph which contained an All-Tech S-5 column.

Results and Discussion

The electronic absorption spectrum of a 10^{-4} M solution of $Pd(PPh_3)_2O_2$ in dichloromethane is shown in Figure 1. The spectrum contains a shoulder at 335 nm on the long-wavelength side of the massive ligand-centered transitions at higher energies.

Photolysis of a 10^{-4} M solution of $Pd(PPh_3)_2O_2$ in dichloromethane for 20 min using 405- or 366-nm light did not produce any spectral changes. However, when a 1:2 mixture of $PdL_2O_2:PPh_3$ in CH_2Cl_2 was photolyzed, the spectral changes shown in Figure 1 were observed. As the photolysis progressed, a sharp peak at 345-nm appeared and an isosbestic point was found at 318 nm. The isobestic point remained for the first 25% of this and all other similar reactions.

The photoproduct causing the 345-nm absorption band was identified as *trans*-PdL_2Cl_2. The product was identified by comparing the spectrum of an independently prepared sample of *trans*-PdL_2Cl_2 to that of the photoproduct. The spectroscopic properties agree with the literature values.[12] In addition, a highly concentrated $PdL_2O_2:PPh_3$ solution was photolyzed in order to produce enough of the yellow product for characterization by elemental analysis. The elemental analysis corroborated the characterization of the product as being PdL_2Cl_2. The additional sharp absorption bands in the spectrum at 272, 267, 260, and 255 nm were identified as Ph_3PO absorbances by comparing the positions to the known spectrum.

When PdL_4 was dissolved in an alkyl halide solvent under atmospheric conditions or when the solvent is O_2 saturated, the resulting UV–visible absorption spectrum contained the characteristic absorption shoulder at 335 nm. (The absorption occurred in all solvents used including pure benzene.) Photolysis of the solutions produced PdL_2Cl_2 as in the $PdL_2O_2:PPh_3$ case.

Photolysis of PdL_2O_2 for 20 min using light of wavelength greater than 500 nm produced no apparent photoreaction. Weak d–d absorption bands occur in the 600-nm region of the spectrum. The photoreaction observed with use of 405-nm irradiation probably arises from a charge-transfer excited state. The 335-nm absorption band in PdL_2O_2 is assigned to the ligand to metal charge-transfer band calculated by Norman to occur at 335 nm in the analogous platinum compound.[13]

The quantum yields under the different conditions are shown in Table I. In all cases, the quantum yields are the same within experimental error.

When PdL_4 was dissolved in degassed CH_2Cl_2, the resulting absorption spectrum contained a sharp peak at 315 nm on the long-wavelength side of the intense ligand-centered absorptions but no shoulder at 335 nm. With the slow addition of oxygen, the 313-nm peak gradually decreased and the shoulder at 335 nm appeared and gained intensity. Irradiation at 366 or 405 nm of the degassed solution immediately after oxygen was added had no effect on the rate of increase of the 335-nm shoulder relative to that of the normal reaction. The subsequent illumination of the thermally stabilized oxygenated solution produced PdL_2Cl_2 and PPh_3O as in the other cases.

The species producing the 315-nm peak when PdL_4 is dissolved in a carefully degassed solvent is most probably PdL_3. Monn and Musco's ^{31}P studies indicated that PdL_4 dissociates into PdL_3 and L in solution.[14]

Both $Pd(PMePh_2)_4$ and $Pd(diphos)_2$ were subjected to the same photolysis conditions as $Pd(PPh_3)_4$. Under atmospheric conditions, $Pd(PMePh_2)_4$ showed a shoulder at 320 nm indicative of an O_2 complex. Subsequent illumination caused the growth of a peak at 335 nm from the corresponding PdL_2Cl_2 complex. Stability problems precluded any quantum yield measurements of the reactions of $Pd(PMePh_2)_4$. Because $Pd(diphos)_2$ showed much lower photoactivity, no isosbestic points, and no clear-cut product absorption band, quantum yields were not measured.

Thermal reactions were minor but not negligible during the time required for photolysis in most solvents. In 1,2-dichloroethane and $CHCl_3$, thermal reactions producing *trans*-$Pd(PPh_3)_2Cl_2$ proceeded about a third to a half as fast as the photochemical reaction. The thermal rate was taken into account when calculating quantum yields. With initially degassed and cleaned solvents, the thermal reaction slowly produced PdL_2Cl_2 at room temperature. Under atmospheric conditions, a different thermal reaction produced an unidentified bright orange compound which had a broad absorption band at 450 nm. Ultimately this pathway leads to precipitation of Pd metal.[15] When the PdL_2O_2 solution was irradiated under atmospheric conditions, no 450-nm absorption band was observed.

In order to determine if singlet O_2 was produced during the reaction, we added 1-methylcyclohexane, a singlet oxygen trapping agent,[11] to benzene or acetonitrile solutions containing PdL_2O_2 and $PdL_2O_2 + 2L$. The solution was photolyzed for 2 h, and the photoproducts were analyzed with the use of a gas chromatograph. No photoproducts characteristic of singlet oxygen reactions were detected, indicating that singlet oxygen is not produced during photolysis of PdL_2O_2.

The photochemical results reported here are consistent with the mechanism given in eq 1–5. The photoproduction of

$$PdL_4 \rightarrow PdL_3 + L \qquad (1)$$

$$PdL_3 + O_2 \rightarrow PdL_2O_2 + L \qquad (2)$$

$$PdL_2O_2 \xrightarrow{h\nu} PdL_2O_2^* \qquad (3)$$

$$[PdL_2O_2]^* + 2L \rightarrow PdL_2 + 2LO \qquad (4)$$

$$PdL_2 + \text{alkyl halide} \rightarrow PdL_2Cl_2 \qquad (5)$$

triphenylphosphine oxide and the requirement that excess triphenylphosphine be present are similar to the results of Halpern et al. on the thermal production of Ph_3PO by PtL_3 through a PtL_2O_2 intermediate.[16,17] In the thermal mechanism, excess L is also required. In the presence of excess $AsPh_3$ or $PMePh_2$, photolysis of $Pd(PPh_3)_2O_2$ produced $PdLL'Cl_2$ or PdL'_2Cl_2 photoproducts as evidenced by new absorption bands

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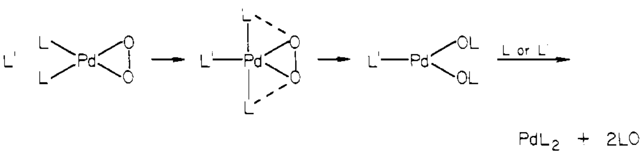
at 355 and 330 nm, respectively.

Step 4 in the proposed mechanism is probably a composite of several reactions which are not completely determinable by our photochemical results. The presence of L′ ligands on the *trans*-dichloropalladium(II) photoproduct in solutions containing excess L′ could be explained by a mechanism similar to that proposed by Halpern for thermal reactions of platinum.[17]



Acknowledgment. The support of the National Science Foundation and a Camille and Henry Dreyfus Teacher-Scholar Award (to J.I.Z.) are gratefully acknowledged. We thank Professor C. S. Foote for assistance in the tests for singlet oxygen.

Registry No. $Pd(PPh_3)_2O_2$, 29933-60-6; $Pd(PPh_2Me)_2O_2$, 78591-75-0; $Pd(PPh_3)_4$, 14221-02-4; $Pd(PPh_2Me)_4$, 24981-80-4; $Pd(PPh_3)_2Cl_2$, 28966-81-6; $Pd(PPh_2Me)_2Cl_2$, 26973-01-3; O_2, 7782-44-7.

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Solvent Effects on the Valence Isomerization Catalyst (Norbornadiene)rhodium Chloride Dimer

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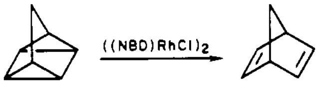
Received November 26, 1980

The valence isomerization of quadricyclane (eq 1) has been shown to be catalyzed by a myriad of metal complexes, including $((NBD)RhCl)_2$.[1]



1 2 (1)

Hogeveen and Volger[1b] were the first investigators to report on the reaction using $((NBD)RhCl)_2$. Subsequently, Halpern[1e] reported rate constants for the same isomerization of 1.9 and 2.1 $M^{-1}\ s^{-1}$ (40 °C) in CCl_4 and $CDCl_3$, respectively. He also reported that the reaction was not inhibited by the product norbornadiene (NBD). This was particularly interesting in light of the fact that Volger[2] had shown earlier that the rhodium dimer, **3**, was cleaved by NBD in $CDCl_3$–CD_2Cl_2 to a monomeric rhodium complex, **4** (eq 2). Extrapolation of

$$\underset{\mathbf{3}}{((NBD)RhCl)_2} + 2NBD \rightleftarrows \underset{\mathbf{4}}{2(NBD)_2RhCl} \qquad (2)$$

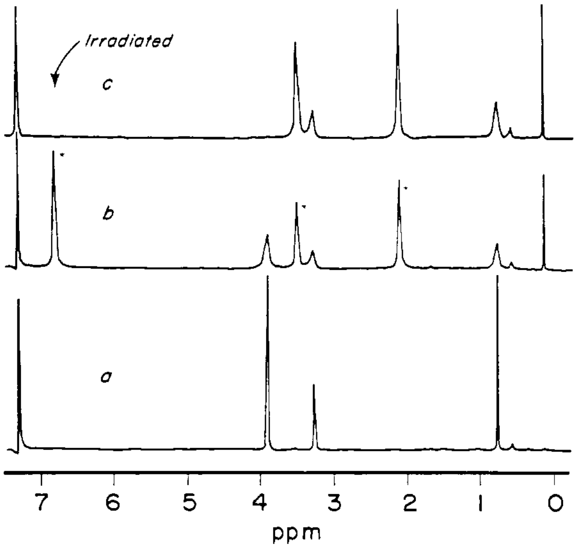


Figure 1. NMR spectra at 250 MHz of $((NBD)RhCl)_2$ in benzene at 25 °C: (a) rhodium complex alone; (b) rhodium complex and norbornadiene (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed NBD; (*) resonances attributed to uncomplexed NBD.

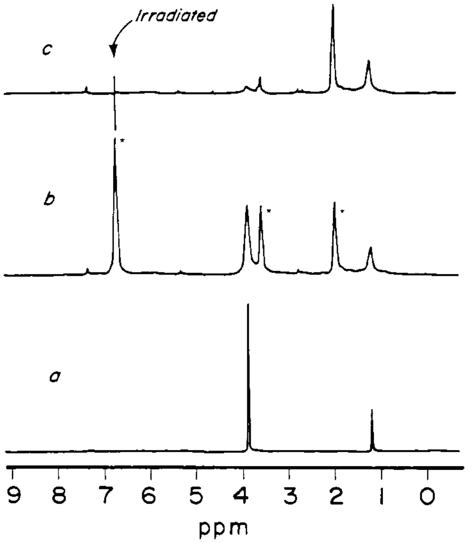


Figure 2. NMR spectra at 250 MHz of $((NBD)RhCl)_2$ in CCl_4 at 25 °C: (a) rhodium complex alone; (b) rhodium complex and norbornadiene (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed NBD; (*) resonances attributed to uncomplexed NBD.

Volger's equilibrium data to 40 °C, the temperature of Halpern's kinetic experiment, revealed that a mixture of dimeric and monomeric rhodium complexes would be changing during the course of the reaction ($K^{40\,°C} = 0.1\ M^{-1}$).

The results herein reported show that a new equilibrium constant is warranted on the basis of the revised NMR assignments for monomer **4**. The new equilibrium constants are used to explain both the lack of an NBD effect on the rate constant at 40 °C and an enhanced rate constant at 1 °C from NBD.

Results

Characterization of Solvents Effects on $((NBD)RhCl)_2$. In this investigation, the characteristics of the rhodium complex were determined in $CDCl_3$, CCl_4, and benzene. Vapor-phase osmometry (VPO) and NMR spectroscopy studies showed that the integrity of the dimeric rhodium complex is preserved in each solvent at 25 °C in the absence of NBD (Figures 1a, 2a,

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(3) For reasons not known to us, saturation of the olefinic resonances of uncomplexed NBD saturate both the olefinic proton resonance of bound NBD and the bridgehead resonance of free NBD.

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